

## Characterization of Upgraded Coal Liquids

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### INTRODUCTION

The upgrading of coal liquids has become necessary in order to make acceptable fuels for home, transportation and industrial use. Several research groups have stepped up their activities in coal liquid upgrading, as evidenced by a recent symposium (1). However, only a few studies have been reported on characterization and structural analysis of the different fractions obtained in the upgrading of coal-derived liquids.

In this study, upgraded coal liquids from a blend of 30 weight percent of SRC I with 70 weight percent of SRC II, as well as from SRC II, have been studied by IR and NMR techniques. The variation of structural parameters of the upgraded liquids has been determined as a function of reaction temperature and contact time in the catalytic hydroprocessing. The results indicate that along with the decrease in heteroatom contents, asphaltene content, aromatic content and a corresponding increase in aliphatic content, the hydrogen-bonded structure and phenolic OH content of the coal liquids drastically decrease with increase in contact time and temperature. The disappearance of phenolic OH in upgrading process follows a first-order kinetics but no such dependence was observed in case of acidic NH.

### EXPERIMENTAL

SRC I and SRC II were made from Kentucky bituminous coal. SRC II was a liquid product with initial boiling point of 453 K and extending into end boiling point of 665K. Elemental analysis of the two products are listed in Table I, with the results of solvent fractionation based on solubility in toluene and pentane. The blend was prepared by adding 30 parts SRC I to 70 parts SRC II by weight at 413-423 K for 2.5 hrs. under nitrogen pressure.

SRC II and the blend were hydroprocessed over a Ni-Mo catalyst (Nalco NM504) in a trickle bed reactor at hydrogen pressure of 13.8 MPa, liquid hourly space velocities (LHSV) of 0.5, 0.75, and 1.0 hr<sup>-1</sup>, and temperatures of 672 and 694 K. Prior to the hydroprocessing, the catalyst in the oxide form was presulfided with a H<sub>2</sub>/H<sub>2</sub>S stream. The hydroprocessing experiments were carried out during a 32-hour continuous operation.

Infrared spectra were recorded on solutions in CS<sub>2</sub> in a 5-mm KBr liquid cell with the solvent in the compensating beam on a Beckman IR-20 infrared spectrometer. The NMR structural parameters (2) were determined before and after hydroprocessing by using a 60-MHz FT NMR spectrometer (Perkin-Elmer R-600).

## RESULTS AND DISCUSSION

Several properties, including the results of elemental analysis and solvent analysis for the two kinds of feed materials and their upgraded liquids, are listed in Table 2. The blend and SRC II are sometimes referred as F-1 and F-2, respectively. Hydroprocessed liquids from F-1 are referred as U-1 to U-4, while the upgraded liquid from F-2 is referred as U-5, according to the various hydro-processing reaction conditions as shown in Table 2. With F-1 as feedstock, increase in the H/C ratio is found with increase in contact time at 672 K, but a satisfactory increase in H/C can be obtained at higher temperature of 694 K. Values of H/C and specific gravity of U-5 are comparable to those of light petroleum crude oils such as Kirkuk and Khafji (H/C: 1.68-1.80; specific gravity: 0.85-0.89). Values of U-4 are comparable to heavy petroleum crude oils such as Eocene and Boscan (H/C ratio: 1.51; specific gravity: 0.95 - 0.99 (3)). N/C ratio decreases with increase in contact time and temperature.

The IR spectra of F-1 and U-4 are shown in Fig. 1. The decrease of hydrogen-bonded structure after upgrading is seen by the dramatic decrease of broad bands of  $3400\text{ cm}^{-1}$  (bonded OH) and  $1610\text{ cm}^{-1}$  for U-4. The intense band of  $1610\text{ cm}^{-1}$  for F-1 is due to the hydrogen-bonded carbonyl stretching in addition to the skeleton vibration of the aromatic ring (4).

Structural parameters were determined from NMR spectra of the coal liquids in  $\text{CS}_2$ . There seems to be no significant difference in the parameters of F-1 and F-2. (Table 3). It should be noted, however, that the  $\text{CS}_2$ -soluble fraction of the blend (F-1) is 89.5% and that the toluene-insoluble fraction of F-1 could not be dissolved in  $\text{CS}_2$ . In using F-1 as feedstock, there is a gradual decrease in  $f_a$  accompanied by an increase in the degree of substitution of aromatic nucleus ( $\sigma$ ), with increase in contact time of hydroprocessing at 672 K. At the higher temperature of 694 K,  $f_a$  of the upgraded oils from F-1 and F-2 were decreased to 0.33 and 0.17, respectively. Table 3 shows that U-5 is mainly composed of aliphatic compounds, and this is supported by the high H/C ratio (Table 2) as well as IR spectra.

Removal of phenolic OH and acidic NH groups in hydroprocessing of SRC liquids was studied kinetically by measuring the intensity of free OH and NH stretching vibrations at  $3600$  and  $3480\text{ cm}^{-1}$ , respectively. The relative decrease of the OH and NH group intensities is summarized in Table 4 in relation to the contact time of hydroprocessing of F-1 at 672 K. The removal of OH group was found to follow first-order kinetics (Fig. 2). However, no such dependence was observed for the NH group. It must be mentioned that the importance of the effect of mass transfer processes or incomplete catalyst wetting has not been considered in this discussion. As shown in Fig. 2, the relative decrease in the N/C ratio also follows a first-order kinetics under the same reaction conditions. The relative reactivity of oxygen removal to nitrogen removal in hydroprocessing of F-1 at 672 K is estimated to be 2:1, from the slopes in Fig. 2.

Fig. 3 shows partial IR spectra of SRC liquids before and after hydroprocessing in rather concentrated  $\text{CS}_2$  solutions of the same concentration (19.2 g/l). After hydroprocessing, the intensity of the  $3600\text{ cm}^{-1}$  peak decreases and new absorption at  $2670\text{ cm}^{-1}$  is found in the upgraded oils. The intensity increases with increase in contact time and temperature of hydroprocessing. The absorption in this region can be ascribed to the proton-transfer NH stretching ( $\text{N}^+ \text{H} \dots \text{O}^-$ ) (5). We have previously found that when an aliphatic amine as triethylamine is added to the acid/neutral fraction of SRC process solvent, new absorptions were found at  $2630$ ,  $2610$  and  $2505\text{ cm}^{-1}$  (6) and we ascribe these to the formation of proton-transfer ionic species, ( $\text{N}^+ \text{H} \dots \text{O}^-$ ). The spectrum of U-5 shows that it contains a certain amount of such species, even after almost complete disappearance of NH stretching at  $3480\text{ cm}^{-1}$ . The implication is that the proton-transfer ionic species are formed under present hydroprocessing conditions.

Table 5 gives the infrared absorbance ratio of  $\text{CH}_3/\text{CH}_2$  for the hydroprocessed liquids in dilute  $\text{CS}_2$  solution. The ratio decreases from 0.87 to 0.56 with increase in contact time of processing at  $672\text{ K}$ , using F-1 as feedstock. The result may indicate that the upgraded oils in the hydroprocessing treatment takes on a saturated cyclic structure (7).

Structural parameters in the asphaltene fractions of the upgraded liquids are given in Table 6. It is interesting to note for the asphaltenes that the values of  $H_{\text{Au}}/\text{Ca}$  actually decrease with increase in contact time of hydroprocessing, whereas the reverse is true for the unfractionated liquids. There is also an increase in the number-average molecular weight of the asphaltenes which are isolated from liquids which have been hydroprocessed with a longer contact time. The changes in properties of the various asphaltenes are particularly intriguing, and we plan further experiments with the asphaltenes.

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Table 1. Elemental and Solvent Analyses of SRC Products

SRC	Elemental Analysis (wt% maf)					atomic H/C ratio	Toluene-insoluble (TI)	Solvent Fractionation Distribution (wt%)		Heavy oil <sup>+</sup> (HO)
	C	H	O	N	S			Asphaltene (A)	Asphaltene <sup>**</sup>	
SRC I	85.6	6.05	5.6*	2.01	0.74	0.84	34.1	48.8	17.1	
SRC II	89.0	8.7	1.16	0.84	0.28	1.17	0.0	0.7	99.3	

\*by difference, \*\*Toluene-soluble and pentane-insoluble, + pentane-soluble

Table 2. Properties of Hydroprocessed SRC Liquids

Upgrading Conditions Temp. LHSV K hr <sup>-1</sup>	Elemental Analysis (wt% maf)				atomic H/C ratio	Solvent Fractionation		Viscosity cp 311 K	Specific Gravity 289/289 K
	C	H	O*	N	S	TI	A		
F-1	87.9	7.95	2.5	1.32	0.3	1.09	1.3	10.2	18.5
U-1	88.9	9.7	0.7	0.61	<0.1	1.31	0.59	1.6	10.9
U-2	89.0	10.1	~0.3	0.50	<0.1	1.36	0.48	0.2	7.4
U-3	89.0	10.4	~0.2	0.24	<0.1	1.40	0.23	0.0	5.1
U-4	88.5	11.3	~0	0.16	0.017	1.53	0.15	0.0	0.5
F-2	89.0	8.7	1.16*	0.84	0.28	1.17	0.81	0.0	0.7
U-5	87.3	12.7	~0	0.02	<0.1	1.75	0.02	0.0	0.1
								120	1.068
								9.5	0.981
								6.1	0.960
								5.2	0.942
								3.0	0.899
								5.0	0.999
								1.5	0.857

\*by difference, \*\*by direct method

Table 3. Structural Parameters for Hydroprocessed SRC Liquids

Sample	Proton Distribution (Area %)			Structural Parameters			
	Aromatic $H_a$	Benzylic $H_\alpha$	Aliphatic $H_o$	$f_a$	$\sigma$	$H_o/H_\alpha + 1$	$H_{au}/C_a$
F-1**	38.9	27.7	33.4	0.66	0.28	2.2	0.93
U-1	21.4	29.7	48.9	0.49	0.42	2.6	0.99
U-2	19.3	28.7	52.0	0.45	0.43	2.8	1.03
U-3	15.7	24.6	59.7	0.41	0.44	3.4	0.97
U-4	12.9	19.6	67.5	0.33	0.43	4.4	1.05
F-2	37.3	29.8	32.9	0.63	0.30	2.1	0.98
U-5	4.6	9.6	85.8	0.17	0.51	9.9	0.98

\*Separation point between  $H_\alpha$  and  $H_o$  chosen at  $\delta = 2.1$  ppm

\*\*Elemental analysis of the  $CS_2$ -soluble fraction of F-1: C 88.2, H 8.3, O 2.0, N 1.18, S 0.3. The  $CS_2$ -soluble fractions of F-1 and U-1 are 89.5% and 99.2%, respectively. All other samples are completely soluble in  $CS_2$ .

Table 4. Reduction of Phenolic (OH) and Acidic Nitrogen (NH) Groups in Hydroprocessing of the Blend of SRC I with SRC II

Sample	Unfractionated Liquid	
	% OH*	% NH*
U-1	19	88
U-2	11	82
U-3	4.4	48

\*% of original OH and NH groups remaining in the upgraded liquids, determined by IR.

Table 5. Infrared absorbance ratio of CH<sub>3</sub>/CH<sub>2</sub> for various hydro-processed SRC liquids.

Sample	F-1	U-1	U-2	U-3	U-4	F-2	U-5
ACH <sub>3</sub> /ACH <sub>2</sub>	0.87	0.62	0.59	0.56	0.57	0.83	0.53

\*Absorbance of symmetrical stretching vibration of

CH<sub>3</sub> group at 2960 cm<sup>-1</sup> : ACH<sub>3</sub>

CH<sub>2</sub> group at 2925 cm<sup>-1</sup> : ACH<sub>2</sub>

Table 6. Structural parameters of asphaltene fractions isolated from upgraded SRC liquids.

Source of Asphaltene	Proton Distribution (Area%)		Structural Parameters					Mol. Wt.
	Aromatic	Aliphatic	Benzyllic	Aliphatic	σ	Ho/H <sub>α</sub> +1	Hau/C <sub>α</sub>	
	Ha	H <sub>α</sub>	Ho	fa				
F-1	37.9	38.1	24.0	0.76	0.40	1.6	0.64	820
U-1	33.9	36.0	30.1	0.75	0.39	1.8	0.57	1130
U-2	34.0	32.0	34.0	0.75	0.36	2.1	0.54	1180
U-3	34.0	32.5	33.5	0.75	0.36	2.0	0.54	1160

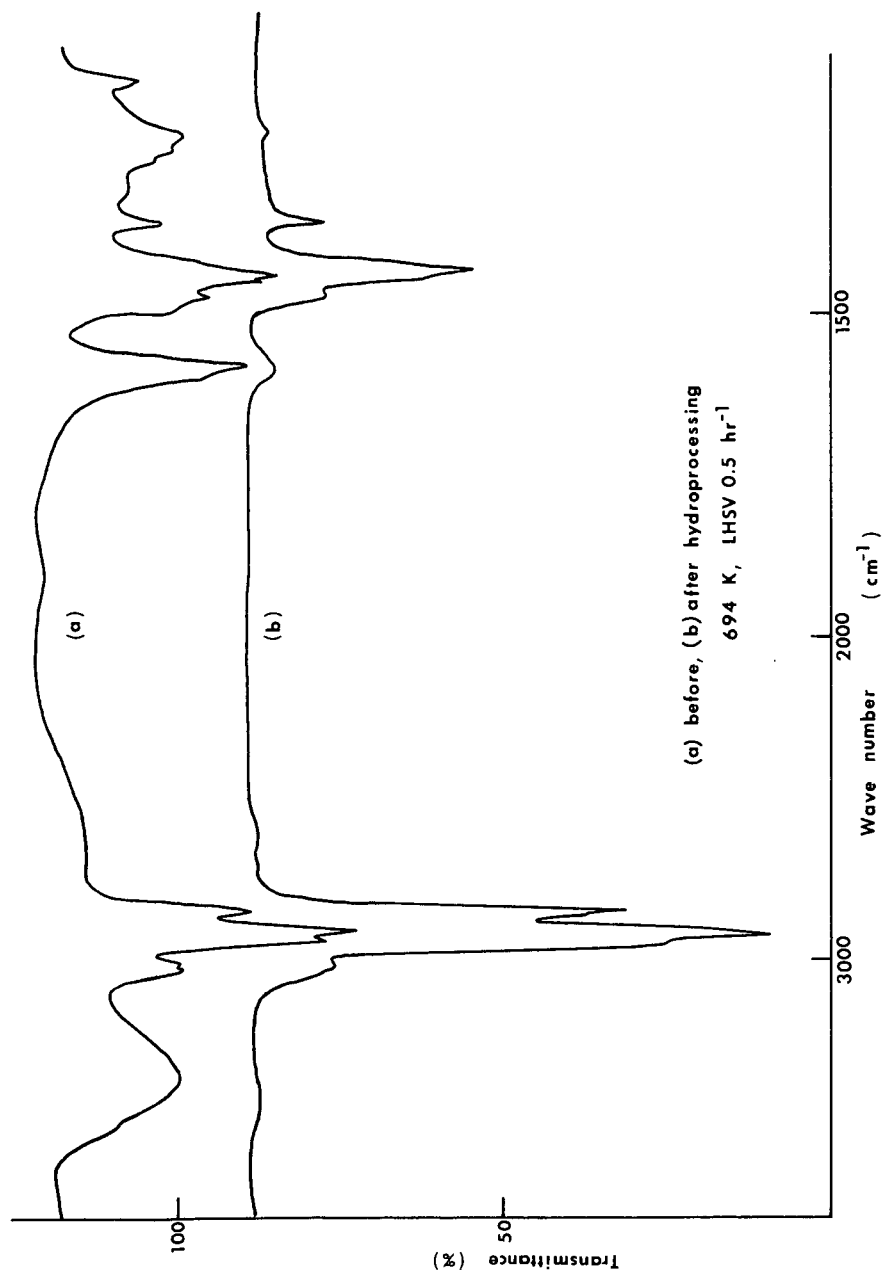


Fig. 1 IR spectra of the blend of SRC I with SRC II before and after upgrading

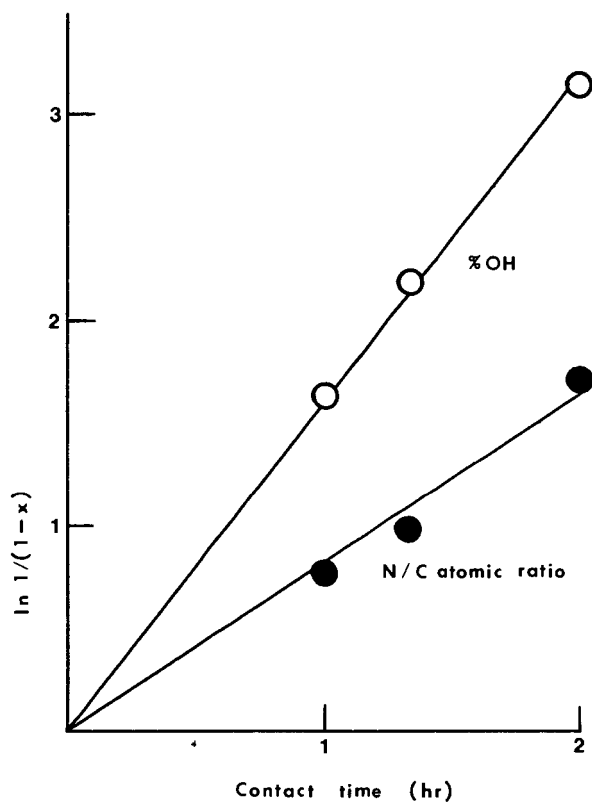


Fig. 2 First-order plot of removal of oxygen and nitrogen

Feed F-1, 672 K  
x % conversion



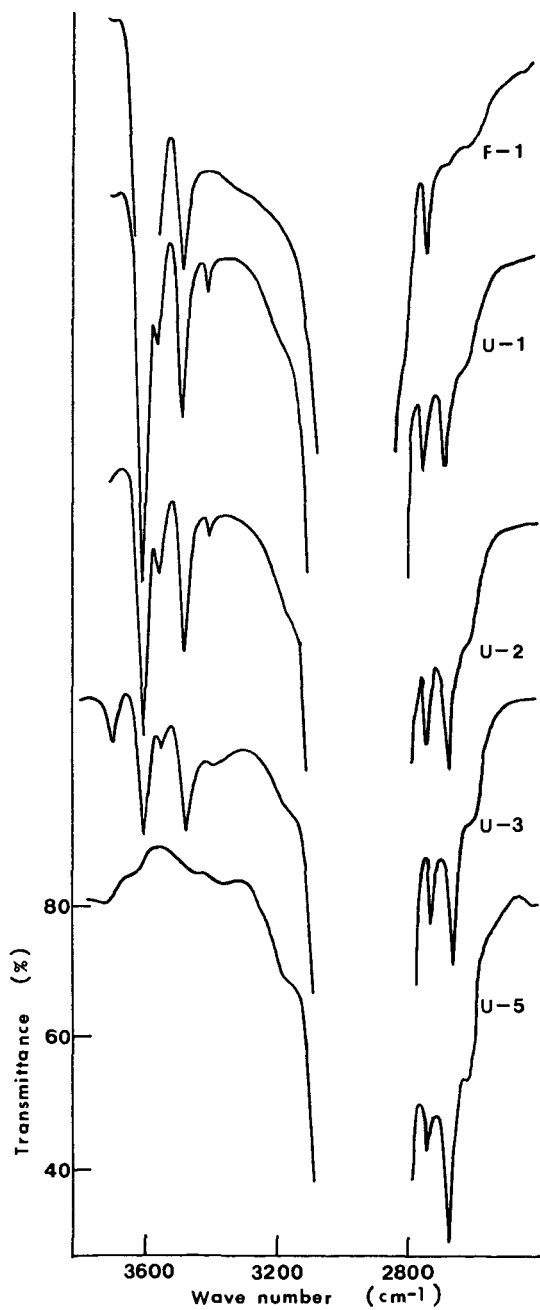


Fig. 3 Formation of proton transfer species ( $\text{NH}^+$ ) in hydroprocessing

Solvent  $\text{CS}_2$ , 19.2 g/l